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USSR DEVELOPMENTS IN RESEARCH ON CATALYSIS

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[Numbers in parentheses refer to appended bibliography.]

In the science of catalysis one may differentiate between three basic problems which, although interdependent, have retained their individual significance and their independent course of development: 1. The problem of the kinetics of catalytic reaction; 2. The problem of producing catalysts which have the most extensive and most stable active surface; and 3. The problem of the nature of catalytic acceleration, i.e., of the catalytic action itself. The ways along which the solution of the first two problems must proceed have been sufficiently established; there is no doubt that by following these ways theory will satisfy to an increasing extent the requirements of practical work in the field of catalysis. The situation is different with regard to the third problem, which involves the very nature of catalytic action and the possibility of selecting on the basis of a sufficient knowledge of the nature of this action the most effective and highly selective catalysts for definite reactions that are thermodynamically feasible.

This cardinal problem of the theory of catalysis is also of the greatest importance from the economic standpoint. It requires a speedy solution for that reason.

There are many different theoretical concepts on the basis of which the nature of catalytic activity is explained, e.g., the theory of intermediate compounds, the theory of ensembles, the multiplet theory, the electron theory, the presorption theory, and the radical-chain theory. The mere fact that there are so many theories pretending to explain all catalytic phenomena indicates that the theory of catalysis is in a very unsatisfactory state. None of the theories mentioned is capable of satisfying practical requirements as far as the solution of the last [third] problem which has been formulated is concerned.

The practical problems of catalysis require that very fine differences between catalysts be determined and established. The discovery of a catalyst the activity of which exceeds that of a known catalyst by a factor of 2-3 represents significant progress. An important advance which often determines whether or not a catalyst can be used is an increase in the selectivity amounting to 10-20%.

The existing theories of catalysis at the best can furnish only the most general ideas on the nature of catalysis. These ideas are entirely inadequate for the solution of problems involved in the selection and improvement of catalysts. It is true that some contemporary theories of catalysis not only attempt to explain qualitatively the elementary catalytic action, but also demonstrate in principle how the acceleration effected by the catalyst can be calculated quantitatively. For instance, A. A. Balandin (1) in his multiplet theory of catalysis uses for the calculation of the energy of activation of a catalytic doublet reaction of the type



the expression

$$\varepsilon \approx 0.75E; E = -Q_{AB} - Q_{CD} + Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK} + (a'-a) + (b'-b) + (c'-c) + (d'-d) + \lambda$$

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where  $Q$  with the corresponding indexes represents the energies of combination of atoms A, B, C, and D with each other and with the catalyst atoms K;  $a$ ,  $b$ ,  $c$ , and  $d$  are corrections for the effect of substituents in molecules on the values of  $Q$  (with a "prime" superscript in a free molecule and without a superscript in a molecule bound to the catalyst); and  $\lambda$  a correction for the effect exerted by catalyst atoms located in the vicinity of an active center.

None of these corrections can be uniquely determined. But even if a unique determination should succeed in some particular case of the simplest type, the inadequately substantiated approximate relation between  $\epsilon$  and  $E$  remains. The inexactitude of this relation more than offsets the total magnitude of the difference between catalysts which is being sought. Under the circumstances only a rough qualitative evaluation is possible and results which are of practical use cannot be obtained.

It seems that the way of solving the problem of the effective selection of catalysts which is being pursued by the contemporary science of catalysis is not only futile from the practical standpoint because of the inexactitude of the data which are to be used in the calculations but also inherently erroneous, metaphysical, and misleading.

The methodological shortcoming of the majority of the theoretical conceptions pertaining to catalysis consists in the underlying tendency to regard the catalytic process as the final result and sum total of relatively simple phenomena which have been thoroughly investigated and which consist of physical transformations and ordinary chemical reactions that form stages of the total process. Occasionally one even encounters an expression of the opinion that when the actual mechanism of catalytic reactions has been clarified, the concept of catalysis will become superfluous, because catalytic reactions are not basically different from ordinary reactions proceeding in stages and are regarded as catalytic only for the reason that sufficient knowledge of some of the stages is lacking.

Ideas of this sort have determined the direction in which work on the theory of catalysis has proceeded during the past few decades, so that the research which has been done was concentrated on elementary reactions. While a knowledge of the elementary reactions and of the adsorption phenomena which occur is essential for a correct understanding of the catalytic process, it is inadequate for the formulation of a true theory of catalysis, because the specificity and the unique character of the catalytic phenomena are not reflected in the processes studied.

It is true, of course, that the catalytic process is first of all a chemical transformation. Nevertheless, catalysis implies a specific course of chemical reactions which is qualitatively different from the ordinary course described in classical kinetics. One must find out which of the essential characteristics of the catalytic phenomenon determine its specificity and in what respects the catalytic process differs from an ordinary chemical reaction. Occurrence of stages in the reaction (the theory of intermediate compounds), adsorption of various types (adsorption theories), and the inhomogeneity of the surface on which the reaction takes place (the theory of active centers) are important characteristics that are typical for the course of catalytic reactions. However, all of these characteristics are also typical for ordinary, noncatalytic heterogeneous reactions. They do not determine the specific nature of the catalytic process.

A characteristic trait of catalysis is the obligatory presence of a competing substance in the chemical interaction of the catalyst with one of the reagents, so that the process initiated by the catalyst ends without inclusion of the catalyst into the products of even this elementary stage of the reaction.

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Kinetically, a necessary prerequisite for this is the existence of a typical divergence between the facility with which the catalyst interacts with the initial substances participating in the reaction and the thermodynamic instability of the products of this interaction as compared with the products of the catalyzed reaction. Even if it will be possible to investigate completely every possible reaction of the substances with the catalyst, the nature of catalysis cannot be completely uncovered unless the mutual effect of these simultaneous reactions on each will be understood and correctly evaluated, because it is precisely this phenomenon of mutual interaction which constitutes the difference between an ordinary chemical reaction proceeding in stages and a catalytic process.

The thoroughly investigated catalytic reaction of the oxidation of carbon monoxide with oxygen over cupric oxide may serve as an illustration. This reaction can be carried out in separate stages. At the ordinary temperatures of catalysis carbon monoxide reduces cupric oxide relatively easily, becoming oxidized to carbon dioxide. The finely dispersed copper which has formed is reoxidized by the oxygen at the same temperature to cupric oxide. Quantitative data on each of these two individual reactions can be obtained. It would seem that when both carbon monoxide and oxygen are led over the catalyst, both reactions must occur and add up to the catalytic reaction, so that exact data on the individual stages would enable one to describe the total process quantitatively.

We carried out a thorough investigation of this reaction at our laboratory with the aid of tracer atoms.<sup>(2)</sup> Our investigation showed that in the catalytic reaction the exchange of oxygen between cupric oxide and the gaseous phase, which would be normally expected if the reaction proceeded by stages, is absent. Thus when carbon monoxide and oxygen are present together at the surface of a catalyst, their behavior is different from that which they exhibit when present separately.

In such theories of catalysis as the theory of intermediate compounds and the variants of the adsorption theories, the characteristic trait of catalysis which has just been pointed out is disregarded. The catalytic process is assumed to be a sequence of independent stages separate in time which exert no mutual influence on each other and are connected with each other only by reason of the fact that the same agents participate in them. In the more perfect theories, namely the multiplet, electron, and presorption theories, this mutual influence has already been taken into consideration to a more or less pronounced extent. Furthermore, the chief difference between these theories consists in the manner in which they treat this phenomenon: according to the multiplet theory, the transformation of the reaction of the substances with the catalyst into a reaction of the substances with each other proceeds by the formation of a mutual active complex comprising the molecules of the reacting substances and the atoms of the active center of the catalyst; according to the electron theory, the molecules adsorbed at the surface of the catalyst exert an influence on the reaction of the catalyst with the molecules of another substance, this influence being transmitted over a distance through the electron system of the catalyst; while according to the presorption theory, the reaction of one of the substances with the catalyst is interrupted by a collision with the molecule of another reacting substance coming out of the space adjacent to the catalyst. Nevertheless, the phenomenon under consideration is not emphasized in these theories as a specific characteristic of catalysis and becomes lost among other characteristics of the process which, although significant, are not typical for catalysis.

The specificity of the phenomenon and its qualitative difference from other known phenomena such as the consecutive occurrence of elementary states of a chemical reaction, the fact that physical and activated adsorption of the

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initial substances and the reaction products take place, etc., make us abandon the hope that it will be possible to obtain sufficiently precise quantitative data on catalysis by using quantitative data obtained in the study of simple component processes.

Notwithstanding the importance of theoretical physics and physical methods of investigation in chemistry, chemical methods are primarily used in chemical research. In accordance with this principle, catalytic phenomena should be investigated as such rather than from the standpoint of adsorption, desorption, chemical interaction of the catalyst with the reacting substances taken separately, etc.

To create a true theory of catalysis it is necessary first of all to establish the basic principles in accordance with which catalytic processes can be systematized as independent chemical phenomena, and then carry out this systematization. Very little attention has been paid to this aspect of the problem before. Only in recent years have the first attempts at a classification been made, primarily in work done by Soviet scientists, i.e., A. A. Balandin (3), S. Z. Roginskiy (4), and G. K. Boreskov. (5) However, these attempts have not gone far enough as yet.

What are the obstacles which prevent the creation of a rational systematization in the field of catalysis? One of the reasons, i.e., the expectation that it would be possible to solve the principal problems of catalysis by concentrating on the study of elementary states of the simplest model reactions, has been mentioned already.

Because of the tendency to seek a solution along these lines, the huge amount of data collected by plant laboratories and specialized branch laboratories has been neglected. There is still no clarity as far as the problem of an expedient characterization of catalysts is concerned. A characteristic such as the activity of catalysts, with which one frequently operates, is quite nebulous and far removed from quantitative precision. There is no precision in the definition of such concepts as the heat of activation and energy of activation of catalytic reactions; the very concept of reaction velocity requires further precision. The methods for testing of catalysts and the investigation of the kinetics of catalytic reactions are quite unsatisfactory. Because of this the distorting effects of various secondary factors have been often neglected, so that data obtained in different laboratories often show no quantitative correspondence and the results of much of the experimental work that has been done are unreliable.

All this makes the classification and systematization of catalytic processes and of catalysts very difficult. For that reason the most pressing task of workers in this field must be application of more precise methods of experimental investigation. Much has been done along these lines in recent years.

The following significant results have been achieved during recent years in work on the kinetics of heterogeneous catalysis: development of the flow-circulation method at the Institute of Physical Chemistry imeni Karpov, which makes it possible to obtain experimental data on reaction kinetics under more rigidly defined conditions and in a form which is convenient for subsequent use (6); the methods of diaphragms (7) and of individual granules (8) developed at the Institute of Physical Chemistry imeni Pisarzhevskiy, Academy of Sciences Ukrainian SSR, which enable one to evaluate directly and quantitatively the effects exerted by transfer phenomena in heterogeneous catalysis; and work done at the Institute of Physical Chemistry imeni Karpov, which has demonstrated the necessity of measuring the surface of the catalyst being investigated and of referring the kinetic values to a unit of the surface. (9)

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One may hope that the investigations enumerated above and other work that has been done will make it possible to accumulate data on catalytic processes which will be more exact and better suited for theoretical generalizations than those available at present. However, very extensive work must be carried out to accumulate these data. This work cannot be carried out without engaging the collaboration of all specialists in the field of catalysis who are active in theoretical work or employed in work that is being done at specialized branch and plant laboratories. Only in this manner can one collect within a short period of time the data necessary for classification and systematization. The task can be accomplished if standard methods for the testing of catalysts are developed and these methods introduced at all laboratories of the USSR.

The conclusions to be drawn from what has been said above can be summarized as follows:

1. It is necessary to expand the work on the search for and perfection of experimental methods used in research on catalysis and develop standard methods to be applied in the testing of catalysts on a large scale to obtain more precise and more highly differentiated data on them. This would make it possible to use in theoretical research the very extensive empirical data available from plant laboratories and specialized branch laboratories.
2. It is essential to concentrate on the methodology of the science of catalysis. First of all one must subject to a thorough revision those definitions of basic concepts in the fields of kinetics and catalysis the formalism and inexactitude of which interfere with the derivation of general relationships from factual data. One must add further precision to the contents of the theory of catalysis and to its interrelationships with individual hypotheses and special theories pertaining to various aspects of catalysis and types of catalytic action.
3. In work on the theory of catalysis the chief emphasis must be placed on finding a rational basis for the systematization of catalytic reactions and catalysts. The capacity of a theoretical concept pertaining to catalysis to serve as a basis for a scientific classification must be regarded as the principal criterion of the value of this concept.

The fundamental postulates which have been advanced should not be regarded as indicating any inclination to underestimate the significance for the creation of a theory of catalysis of new experimental and theoretical methods of catalyst research, of data on the elementary stages of the catalytic process, of data on the elementary catalytic process as a whole, and of theoretical generalizations made on the basis of such data. It has merely been emphasized that a solution of the basic problem of catalysis which has been discussed cannot result directly from investigations of this type, but only from a correlation of the data obtained in them with carefully selected and checked factual material that embraces the whole diversity of catalytic phenomena and reflects its specific nature to the fullest extent.

A critical selection and systematization of reliable results derived from the huge amount of data which is obtained and accumulated every year, the creation of a rational classification of catalytic processes and catalysts, and the application of improved methods of research will assure the formulation of a theory of catalysis that will satisfy the requirements put to it by practice.

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